UDC 666.762.93+66.091.3-977

SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF SILICON-NITRIDE CERAMIC MIX USING FERRO-SILICON AND ILMENITE

L. N. Chukhlomina,[1] O. G. Vitushkina,[1,3] and V. I. Vereshchagin[2]

Translated from *Steklo i Keramika*, No. 9, pp. 15 – 18, September, 2010.

The results of an investigation of the high-temperature nitriding of a mixture of ferro-silicon – ilmenite using a complex method of differential-scanning calorimetry are presented. A ceramic mix with the composition Si_3N_4 – TiN – Si_2N_2O – Fe is obtained by the method of self-propagating high-temperature synthesis using as the raw material dust-like ferro-silicon and ilmenite wastes.

Key words: SHS, nitriding, ferro-silicon, ilmenite, differential-scanning calorimetry.

Ceramic materials with new functional properties can be obtained by adjusting the initial materials, introducing special additives, and using the particulars of the technology chosen. The most promising procedure is to use unconventional raw materials and technologies which do not consume substantial amounts of energy. For this reason, it is of great practical interest to use natural mineral raw materials together with the method of self-propagating high-temperature synthesis (SHS). Among the advantages of this method are low energy consumption and high productivity.

Special attention is devoted to obtaining multiphase composite ceramic materials based on silicon nitride: Si_3N_4 – SiC, Si_3N_4 – TiN, Si_3N_4 – ZrO_2, Si_3N_4 – Al_2O_3, and others. For example, materials of the system Si_3N_4 – ZrO_2 are distinguished by high resistance to oxidation and heat-resistance [1, 2]; materials of the system Si_3N_4 – TiN are electrical insulators or conductors, depending on the titanium nitride content [3].

The conventional technology for obtaining composite materials in the systems Si_3N_4 – ZrO_2 and Si_3N_4 – TiN is based on the use of presynthesized powders of silicon and titanium nitrides as well as zirconium dioxide. Next, the prepared powders are mixed in the required proportions, compacted by one method or another, and sintered.

[1] Division of Structural Macrokinetics of the Tomsk Center for Science at the Siberian Branch of the Russian Academy of Sciences, Tomsk, Russia.
[2] Tomsk National Research Polytechnical University, Tomsk, Russia.
[3] E-mail: liudnik@yandex.ru.

Previous investigations [4, 5] have shown that SHS of silicon nitride is best done using as the raw material iron – silicon (ferro-silicon) alloy, since for otherwise equal conditions the degree of nitriding of the products of combustion of ferro-silicon in nitrogen is higher than with the use of silicon. In addition, ferro-silicon consists of wastes from the production of iron alloys (process dust, arising when ferro-silicon is crushed).

The heat released when ferro-silicon undergoes combustion is sufficient for realizing synthesis of other refractory compounds, occurring by means of energy-consuming reactions, for example using the natural raw material — zircon [6].

The present work presents the results of investigations of directed synthesis of ceramic powders containing silicon and titanium nitrides, and physical-chemical processes occurring with SHS-nitriding of a mixture of ferro-silicon with ilmenite.

Ferro-silicon (PUD-25 grade) and an ilmenite concentrate — a product of enrichment of zirconium – ilmenite alluvial deposits in the Tuganskoe deposit of Tomsk Oblast' — were used as the initial materials. Ferro-silicon is a polydisperse powder with particle size less than 160 μm and silicon content 82.0%.[4] x-ray phase analysis shows the alloy to be two-phase and to consist of silicon and high-temperature lebeauite $FeSi_2$. Ilmenite is a mineral with composition $FeTiO_3$, consisting of a mixture of titanium TiO_2 and iron FeO oxides. In Russia ilmenite concentrates are used mainly as a raw material to produce titanium dioxide and titanium as a well as to obtain ferro-titanium. Ilmenite was used in the

[4] Here and below, unless otherwise state, content by weight.

0361-7610/11/0910-0277

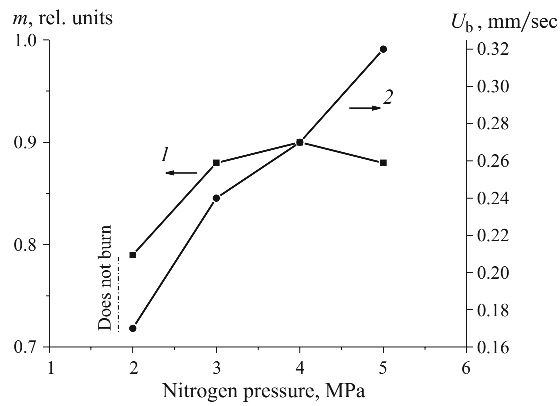

Fig. 1. The degree of nitriding (*1*) and rate of combustion (*2*) of a mixture (45% ferro-silicon, 25% ilmenite, 30% pre-nitrided ferro-silicon) versus the nitrogen pressure.

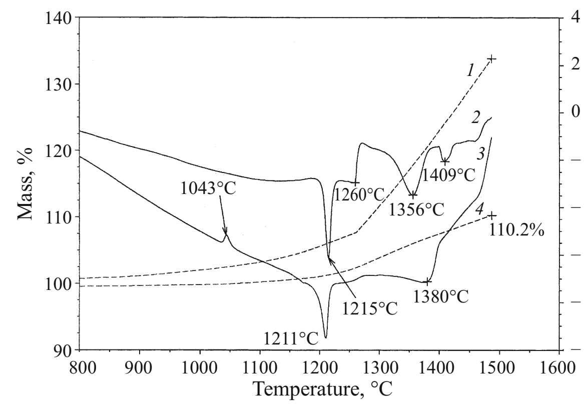

Fig. 2. TG (*1*, *4*) and DSC (*2*, *3*) curves of complex thermal analysis of ferro-silicon powder (*1*, *2*) and powder of ferro-silicon with 30% ilmenite added (*4*, *3*) in nitrogen.

form of a powder with particle size less than 40 μm and titanium dioxide content 62.10% (the remaining iron oxide and impurities following TU 1715-001-58914756–2005).

Before the SHS process was conducted the initial ferro-silicon and ilmenite powders were dried at temperature 150 – 200°C to remove moisture and volatile impurities. To prepare the mix the individual components were mixed in the required ratios after which the mix was poured into a gas-permeable tube and burned in a constant-pressure setup in a nitrogen gas atmosphere (GOST 9293–74) with 99.996% (by volume) nitrogen content. X-ray phase analysis (XPA) was performed with a DRON-2 diffractometer using Co radiation. Thermal analysis was performed with a SDT Q 600 (TA instruments, USA, 2005) combined DSC – DTA – TG – DTG analyzer. The rate of heating of the sample was 20 K/min. The weighed amount of powder used was 10 – 12 mg.

Experimental studies of the effect of the main parameters of synthesis (mixture composition, nitrogen pressure, and sample diameter) on the mechanisms of the combustion of the ferro-silicon – ilmenite mixture shows that as the amount of the ilmenite additive increases, the production of combustion decreases because of the formation of a substantial amount of melt, resulting in filtration difficulties for nitrogen delivery to the reaction zone. A wave of combustion of the melt forms as a result of the melting of ferro-silicon at 1206°C and ilmenite at 1365°C.

Pre-nitrided ferro-silicon was added in amounts 30 – 35% into the initial ferro-silicon – ilmenite mixture in order to increase the degree of nitriding. As pressure increases, the combustion rate and degree of nitriding increase (Fig. 1) because of the increasing rate of nitrogen delivery to the reaction zone. The maximum nitriding is reached with nitrogen pressure 4 MPa for 50 mm in diameter samples.

The maximum temperature of combustion of ferro-silicon in nitrogen in the presence of ilmenite (according to measurements) is 2060 ± 50°C. The combustion temperature is determined by the equilibrium silicon nitride and its products of dissociation — silicon and nitrogen.

Differential scanning calorimetry (DSC) was used to study the process of combustion of the mixture ferro-silicon – ilmenite. This method makes it possible to record the ongoing physical and chemical processes, accompanied by exo- or endothermal effects. Weighed portions of ferro-silicon and ferro-silicon with 30% ilmenite added were heated in a nitrogen atmosphere to 1500°C. The results of these studies are presented in Fig. 2.

Endothermal effects are observed at temperatures 1215, 1356, and 1409°C on the DSC curve *2* during nitriding of ferro-silicon. The endothermal effect with a maximum at temperature 1215°C refers to melting of the eutectic $FeSi_2$ – Si, and the endothermal effects at 1356 and 1409°C belong to the phase transformations in the system Fe – Si in accordance with the phase diagram [7]. The process of active nitriding starts at temperature above 1260°C, as is evidenced by the sharp rise in the curve *2* and the corresponding increase of the mass of the sample due to the nitrogen absorption on the TG curve *1*.

When ilmenite is introduced into ferro-silicon an exothermal effect is recorded at 1043°C on the DSC curve *3*. The exothermal effect corresponds to nitriding of the impurity phase of silicon dioxide SiO_2, which is present in ilmenite. According to [8] nitriding SiO_2 occurs with formation of silicon oxynitride Si_2N_2O, which is synthesized via the formation of silicon mono-oxide SiO according to the following scheme:

$$SiO_2 + Si \rightarrow 2SiO_{(gas)}; \quad (1)$$

$$2SiO_{(gas)} + N_2 \rightarrow Si_2N_2O + \frac{1}{2}O_2. \quad (2)$$

It should be noted that the magnitude of the exothermal effect on the DSC curve at 1054°C increases in a regular manner with increasing ilmenite concentration in the mixture. In addition to an exothermal effect two endothermal effects are recorded at 1211 and 1380°C on the DSC curve *3*. The endothermal effect at 1211°C corresponds to the melting

of the eutectic $FeSi_2$ – Si, and the wide endothermal effect at 1380°C refers to the melting of ilmenite in accordance with the phase diagram [9].

Analysis of the thermogravimetric curve showed that the nitriding of the mixture ferro-silicon – ilmenite is accompanied by weaker absorption of nitrogen (110.2%, curve *4*) than ferro-silicon without ilmenite (133.9%, curve *1*). The experiments on SHS nitriding of ferro-silicon with ilmenite additions also established that that the degree of nitriding decreases with increasing additions of ilmenite. The reason is that ilmenite melts at 1380°C, resulting in filtration difficulties for delivering nitrogen to the reaction zone.

It is shown in [6] that when a ferro-silicon – zircon mixture undergoes nitriding the heat released in the nitride-formation reaction induces an endothermal process of dissociation of zircon, which is accompanied by the formation of its constituent components ZrO_2 and SiO_2. A similar phenomenon is also observed with nitriding of ferro-silicon in the presence of ilmenite. The heat release due to the reaction forming silicon nitride induces oxidation-reduction processes with the participation of ilmenite.

When a ferro-silicon-ilmenite mixture undergoes SHS nitriding heat is released as a result of the interaction of silicon with nitrogen via the reaction

$$3Si + 2N_2 \rightarrow Si_3N_4 + 750\text{ kJ}. \qquad (3)$$

Silicon nitride is formed as a result of the interaction of nitrogen of free silicon ($FeSi_2$ + Si) and silicon, formed as a result of the dissociation of iron silicides above 1350°C [4].

When the temperature reaches 1365°C ilmenite melts in accordance with the FeO – TiO_2 phase diagram [9]:

$$FeTiO_3 \rightarrow FeO \cdot TiO_{2(melt)}.$$

In the wave of the combustion reaction wave, the reduction of iron oxide occurs simultaneously with the reduction of TiO_2 (4), (5) and formation of intermetallic compound with titanium FeTi, which facilitates the reduction of titanium dioxide to titanium (6):

$$2TiO_2 + Si_{(Fe-Si,\ melt)} \rightarrow 2TiO + SiO_2; \qquad (4)$$

$$2TiO + Si_{(Fe-Si,\ melt)} \rightarrow 2Ti + SiO_2; \qquad (5)$$

$$2FeO + Si_{(Fe-Si,\ melt)} + 2Ti \rightarrow 2FeTi + SiO_2. \qquad (6)$$

The interaction of silicon dioxide with iron-silicon melt results in the formation of silicon mono-oxide gas via the reaction

$$SiO_2 + Si_{(Fe-Si,\ melt)} \rightarrow 2SiO_{(gas)}. \qquad (7)$$

Silicon monoxide moves to the outer, colder layers of the sample, where it undergoes condensation together with nitriding. The formation of silicon oxynitride with interaction of silicon mono-oxide gas with nitrogen can be represented by the following reactions:

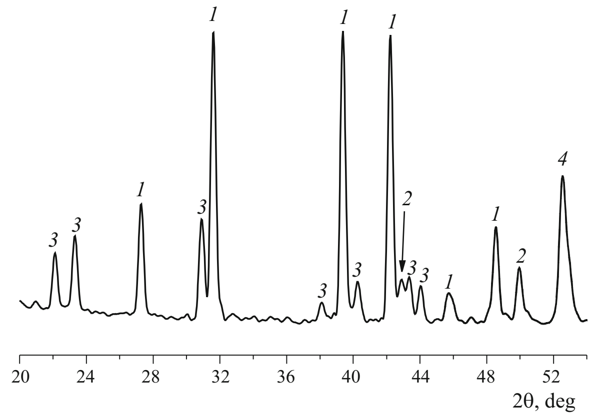

Fig. 3. Fragment of x-ray diffraction pattern of the products of combustion of a mixture (50% ferro-silicon, 30% pre-nitrided ferro-silicon, 20% ilmenite): *1*) β-Si_3N_4; *2*) TiN; *3*) Si_2N_2O; *4*) α-Fe.

$$SiO_2 + Si_3N_4 \rightarrow 2Si_2N_2O \ \ (t > 1610°C); \qquad (8)$$

$$3SiO_{(gas)} + Si_3N_4 + N_2 \rightarrow 3Si_2N_2O \ \ (t < 1750°C); \qquad (9)$$

$$2SiO_{(gas)} + N_2 \rightarrow Si_2N_2O + \frac{1}{2}O_2. \qquad (10)$$

Decomposition of Si_2N_2O with formation of β-Si_3N_4 is possible at temperatures above 1750°C [10 – 12] via the scheme

$$3Si_2N_2O \rightarrow \beta\text{-}Si_3N_4 + N_2 + 3SiO_{(gas)}. \qquad (11)$$

XPA showed that introducing 30 – 35% pre-nitrided ferro-silicon into the initial mixture ferro-silicon – ilmenite makes it possible to obtain a ceramic composition consisting of silicon nitride β-Si_3N_4, titanium nitride TiN, silicon oxynitride Si_2N_2O, and iron α-Fe (Fig. 3). Introduction of 15 – 25% ilmenite in the initial mix promotes the formation of titanium nitride in the amounts 5 – 10% in the composition.

Acidic enrichment of the products of combustion yields a composite ceramic powder based on silicon nitride with residual iron content no greater than 0.5%.

CONCLUSIONS

It has been established that the process of nitriding ferro-silicon with ilmenite additions under programmed heating is accompanied by lower absorption of nitrogen (110.2%) than ferro-silicon without ilmenite (133.9%), since ilmenite melts, resulting in filtrational difficulties for nitrogen delivery to the reaction zone.

In the process of nitriding a ferro-silicon – ilmenite mixture the reaction leading to the formation of silicon nitride induces oxidation?reduction processes with ilmenite participa-

tion. Titanium nitride forms as a result of the reduction of ilmenite, and an intermetallic compound with titanium FeTi is formed and undergoes nitriding. The reduction of iron and titanium oxides by silicon is accompanied by the formation of silicon dioxide, which interacts with nitrogen forming silicon oxynitride.

Acidic enrichment of the productions of combustion of a ferro-silicon – ilmenite mixture makes it possible to obtain the ceramic composition Si_3N_4 – TiN – Si_2N_2O with residual iron content no higher than 0.5%.

RFFI provided the financial support for this work (project No. 09-03-00604-a).

REFERENCES

1. N. V. Zhuravleva and E. S. Lukin, "Ceramic based on silicon nitride," *Ogneupory*, No. 1, 6 – 12 (1993).
2. I. M. Finkel'shtein, "Some properties of materials of the system Si_3N_4 – ZrO_2," *Poroshk. Metall.*, No. 6, 96 – 99 (1974).
3. T. A. Lyudvinskaya, "Effect of the initial components and activating additives on the formation process of the composite powder Si_3N_4 – TiN," in: *Proc. of the International Conference on Modern Materials Science: Advances and Problems* [in Russian], Kiev (2005), p. 283.
4. L. N. Chukhlomina, Yu. M. Maksimov, V. D. Kitler, and O. G. Vitushkina, "On the mechanism and characteristics of nitriding of ferro-silicon in the combustion regime," *Fiz. Goreniya Vzryva*, **42**(3), 71 – 78 (2006).
5. L. N. Chukhlomina, "Characteristics of the synthesis of silicon nitride by combustion of iron-silicon alloy in nitrogen," *Zh. Prikl. Khim.*, **80**(11), 1768 – 1771 (2007).
6. L. N. Chukhlomina, O. G. Vitushkina, and Yu. M. Maksimov, "Self-propagating high-temperature synthesis of the composition Si_3N_4 – ZrO_2 using ferro-silicon and zirconium concentrate," *Perspekt. Mater.*, No. 5, 79 – 84 (2008).
7. O. A. Bannykh (ed.), *Phase Diagrams of Binary and Multicomponent Systems Based on Iron* [in Russian], Metallurgiya, Moscow (1986).
8. I. Ya. Guzman, T. N. Purusova, D. N. Poluboyarinov, et al., "Synthesis of silicon oxynitride," *Ogneupory*, No. 2, 41 – 46 (1966).
9. N. A. Toropov, V. P. Barzakovskii, V. V. Lapin, and N. N. Kurtseva, *Phase Diagrams of Silicate Systems* [in Russian], Nauka, Leningrad (1969).
10. H. V. Levis, C. J. Reed, and N. D. Butler, "Pressureless-sintered ceramic based on the compound Si_2N_2," *Mater. Sci. Eng.*, **8**(1), 87 – 94 (1985).
11. P. Rocabois, C. Chatillon, and C. Bernard, "Thermodynamics of the Si – O – N system: I. High-temperature study of the vaporization behavior of silicon nitride by mass spectrometry," *J. Am. Ceram. Soc.*, **79**(5), 1351 – 1360 (1996).
12. P. Rocabois, C. Chatillon, and C. Bernard, "Thermodynamics of the Si – O – N system: II. Stability of Si_2N_2O(s) by high-temperature study mass spectrometry vaporization," *J. Am. Ceram. Soc.*, **79**(5), 1361 – 1365 (1996).